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2014 Environ. Res. Lett. 9 095007

(http://iopscience.iop.org/1748-9326/9/9/095007)

OPEN ACCESS
IOP Publishing
Environmental Research Letters
Environ. Res. Lett. 9 (2014) 095007 (10pp)
doi:10.1088/1748-9326/9/9/095007

Chinese coastal seas are facing heavy atmospheric nitrogen deposition

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Received 29 May 2014, revised 7 July 2014
Accepted for publication 18 August 2014
Published 24 September 2014

Abstract

As the amount of reactive nitrogen (N) generated and emitted increases the amount of N deposition and its contribution to eutrophication or harmful algal blooms in the coastal zones are becoming issues of environmental concern. To quantify N deposition in coastal seas of China we selected six typical coastal sites from North to South in 2011. Concentrations of NH_3, HNO_3, NO_2, particulate NH_4^+ (pNH_4^+) and pNO_3^- ranged from 1.97–4.88, 0.46–1.22, 3.03–7.09, 2.24–4.90 and 1.13–2.63 $\mu g\ N\ m^{-3}$ at Dalian (DL), Changdao (CD), Linshandao (LS), Fenghua (FH), Fuzhou (FZ), and Zhanjiang (ZJ) sites, respectively. Volume-weighted NO_3^-–N and NH_4^+–N concentrations in precipitation varied from 0.46 to 1.67 and 0.47 to 1.31 mg N L^{-1} at the six sites. Dry, wet and total deposition rates of N were 7.8–23.1, 14.2–25.2 and 22.0–44.6 kg N ha^{-1} yr^{-1} across the six coastal sites. Average N dry deposition accounted for 45.4% of the total deposition and NH_3 and pNH_4^+ contributed to 76.6% of the dry deposition. If we extrapolate our total N deposition of 33.9 kg N ha^{-1} yr^{-1} to the whole Chinese coastal sea area (0.40 million km^2), total N deposition amounts to 1.36 Tg N yr^{-1}, a large external N input to surrounding marine ecosystems.

Keywords: reactive N, atmospheric deposition, coastal sea, eutrophication, China

1. Introduction

Human activities have generated increasingly more reactive nitrogen (N) since 1860, the symbolic year of the industrial revolution, because of increased food production and energy consumption worldwide (Galloway *et al* 2008). China is the world's largest consumer of fertilizer N, with annual fertilizer N consumption of about 32 Tg N (Guo *et al* 2010). Power plants and transportation are the important sectors for NO_x emissions in China. During 2000–2010 the installed capacity of thermal power plants and the vehicle population increased by 195% and 300%, respectively (Wang and Hao 2012). All of these human activities have led to large NH_3 and NO_x

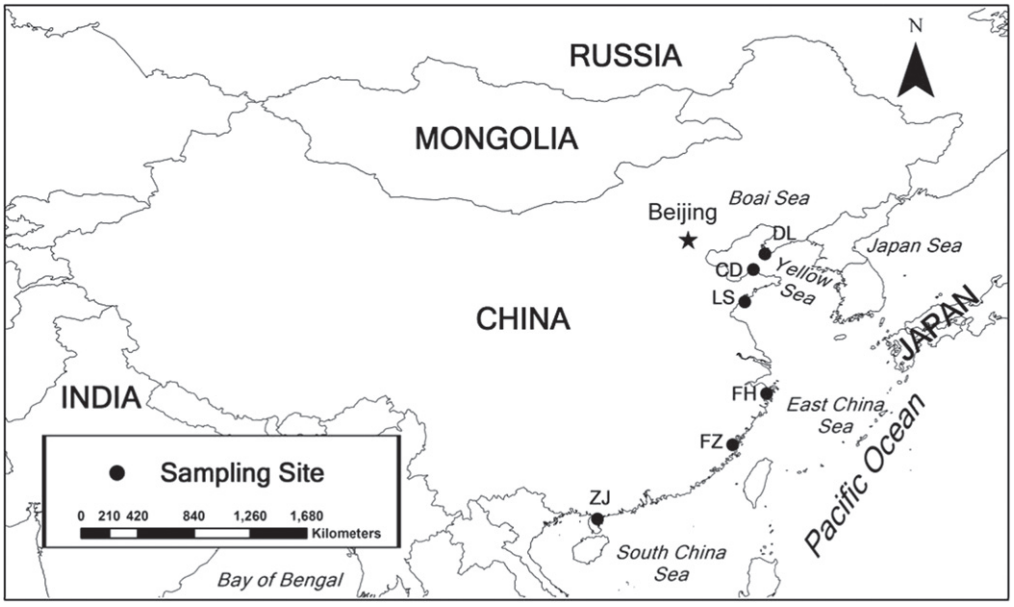

Figure 1. Distribution of the sampling sites along Chinese coastal line in this study.

emissions and have resulted in elevated N deposition especially over the last three decades (Liu *et al* 2013, Cui *et al* 2013). Negative impacts of N deposition include reduction of species diversity and altered biological productivity and soil acidification and eutrophication (Allen *et al* 2011, Erisman *et al* 2013), and have affected the Earth's climate system via direct and indirect pathways (Erisman *et al* 2011). It is therefore important to determine the magnitude of N deposition and predict its impact on the health of different sensitive ecosystems (Rattray and Sievering 2001).

The oceans comprise the largest and most important ecosystems on Earth. The oceans are reactive N emission sources controlled mainly by natural processes and are also important sinks for N deposition (Duce *et al* 2008). Reactive N enters the oceans via rivers, biological N_2 fixation, and atmospheric deposition. As the generation and emission of reactive N have increased, total N deposition to the oceans has more than tripled to ~67 Tg N yr^{-1} in 2000 compared with the value (~20 Tg N yr^{-1}) in 1860 (Duce *et al* 2008). As a consequence, N deposition plays an increasingly important role in the oceans, especially in coastal zones where the N inputs are largest (Seitzinger *et al* 2010). Atmospheric N deposition was found to increase the N abundance of the North Western Pacific Ocean, and the excess N inputs and other elements such as phosphorus (P) have led to eutrophication of the coastal marine ecosystems (Conley *et al* 2009, Kim *et al* 2011). Coastal eutrophication will lead to widespread hypoxia and anoxia, habitat degradation, alteration of food-web structure, loss of biodiversity, and increased frequency, spatial extent and duration of harmful algal blooms (Howarth 2008).

China has long coastlines (total length about 18 000 km). The provinces located in the coastal areas have benefitted enormously from the new economic policies and have made great progress. For example, the GDP of the coastal provinces Guangdong, Shandong, Jiangsu, and Zhejiang are among the top four economically significant regions in China. Economic development also increases activities that release reactive N to the environment. However, studies on the influence of these reactive N emissions on the coastal areas are relatively limited at present. The coasts of China, connecting the mainland of China with the Pacific Ocean and the sources from the mainland are contributing to coastal eutrophication through atmospheric and riverine transport of nutrients (including N). As a result, harmful algal blooms have been observed in the coastal seas (Conley *et al* 2009, Chen *et al* 2011, Liu *et al* 2011). In this study, six coastal sampling sites were set up in China, located at the Bohai Sea, Yellow Sea, East China Sea, and South China Sea. The gaseous and particulate N concentrations and inorganic N concentrations in rain samples were measured and N dry and wet deposition rates to coastal seas were estimated. The objectives of this study were to evaluate the current situation regarding reactive N concentrations and pollution in the air and precipitation of coastal areas and to estimate N dry and wet deposition values and their potential impacts on Chinese marine ecosystems.

2. Materials and methods

2.1. Sampling sites

The study included six sampling sites and all the sampling sites were located in the coastal region (near the sea) or on islands. The sampling sites were set up in Liaoning, Shandong, Zhejiang, Fujian, and Guangdong provinces, respectively (figure 1). The specific sites are Dalian (DL, 38°44′N, 120°31′E), Changdao island (CD, 37°55′N, 124°44′E), Linshan island (LS, 35°45′N, 120°08′E), Fenghua (FH, 29°36′N, 121°31′E), Fuzhou (FZ, 26°10′N, 119°21′E), and Zhanjiang (ZJ, 21°12′N, 110°17′E), respectively. Dalian is a coastal city and is famous for business development. DL is an urban site

Table 1. The start and end sampling periods and total monthly sampling numbers of reactive N and pSO_4^{2-} during the entire sampling period at the six coastal sites.

Site	Sampling period	No. of NH_3	No. of HNO_3	No. of NO_2	No. of pNO_3^-	No. of pNH_4^+	No. of pSO_4^{2-}
DL	September 2010–April 2012	20	20	15	20	20	12
CD	September 2010–June 2012	22	22	19	22	22	17
LS	February 2011–May 2012	15	15	15	15	15	11
FH	August 2010–May 2012	22	22	21	22	22	20
FZ	April 2010–July 2012	28	28	21	28	28	16
ZJ	August 2010–May 2012	22	22	12	22	22	16

where the mean annual temperature is 8–11 °C and the annual rainfall varies between 550 and 1000 mm. DL belongs to the warm temperate and semi-humid monsoon and marine climatic zone. CD is largest island in Shandong province, located in the joint of the Bohai Sea and the Yellow Sea with about 40 000 inhabitants. CD island is remote and does not have industry or agricultural activities near the sampling site. LS is located in the Yellow Sea belonging to Jiaonan city (region), Shandong province. There are about 2700 inhabitants on the island. FH is located in Chunhu town, Fenghua city, Zhejiang province. It is a typical coastal area of the East China Sea and has an advanced fishery. FZ is surrounded by hills and has low population density. The FZ site is surrounded by some agricultural land growing tobacco and paddy rice without large livestock farms or industry. ZJ is located in Leizhou Peninsula, Zhanjiang city, Guangdong province, close to the South China Sea. The climate is tropical with relatively high temperatures, high rainfall, and high plant cover. This area is rich in tropical fruits and farmers use large quantities of fertilizers for fruit production. Although only the DL is located at real urban site, all sampling sites (except FZ) are affected by rapid urbanization (e.g., increased traffic vehicles and population intensities) in coastal area of China. Besides the local N_r sources, all coastal sites receive atmospheric N_r transport from both inland (mainly agricultural sources) and marine (including international ship emissions) ecosystems.

2.2. Equipment for collecting reactive N components and sampling period

Reactive N components were collected by the DELTA (DEnuder for Long-Term Atmospheric Sampling) system which is an active sampling equipment, fulfilling long-time sampling and thus cost saving and it is widely used in the European N deposition monitoring network (Flechard *et al* 2011). Atmospheric HNO_3, NH_3, particulate NO_3^- and NH_4^+ can be captured by the coated wall of the denuders and the subsequent filters. The sampling time is one month. The coating solution is 5% m/v citric acid in methanol for absorbing NH_3, and 1%(m/v) K_2CO_3 + 1%(m/v) glycerol in methanol for collection of HNO_3. The coating solution was 13%(m/v) citric acid in methanol added to the filters absorbing pNH_4^+, and the coating solution which absorbs pNO_3^- is 5%(m/v) K_2CO_3 + 10%(m/v) glycerol in methanol. The extraction solution is 0.05% H_2O_2 for the denuders and filters absorbing NO_3^- (10 ml) and the extraction solution for NH_3 and pNH_4^+ is high purity water (denuders 6 ml and filters 10 ml). The NH_4^+–N and NO_3^-–N concentrations in the samples were analyzed by an AA_3 continuous-flow analyzer (Bran + Luebbe GmbH, Norderstedt, Germany). The DELTA system also absorbs SO_2 and SO_4^{2-} by the denuders and filters. SO_4^{2-} concentration was measured by ion chromatography (761 Compact, Switzerland). Atmospheric concentrations of NO_2 were sampled by passive samplers (UK Environmental Change Network Diffusion tubes) extensively described in Luo *et al* (2013). Monthly reactive N concentrations were collected mostly starting from August or September 2010 and ending in May or June 2012. The detailed sampling periods and the numbers of reactive N and SO_4^{2-} samples at the six sites are listed in table 1.

2.3. Rain water collection and N wet deposition calculation

Rain water samples were collected by precipitation collectors directly after every rainfall event. Wet deposition of N was collected *in situ* by precipitation collectors (SDM6, Tianjin Weather Equipment, China). The sampling period was one complete year (2011). The samples were analyzed for concentration of NH_4^+–N and NO_3^-–N using the AA3 continuous-flow analyzer mentioned above. Wet deposition of NH_4^+–N and NO_3^-–N was then calculated by the following two equations:

N deposition per event (kg N ha^{-1}) = precipitation (mm) × NH_4^+–N or NO_3^-–N concentration in rainwater (mg N L^{-1}) × 0.01.

N deposition per month or year (kg N ha^{-1}) = 0.001 × ∑N deposition per event in a month or year.

2.4. N dry deposition estimation

Compared with wet deposition N dry deposition is relatively complicated because it changes with the meteorological conditions and the surface characteristics. In the inferential model the dry deposition flux can be expressed by

$$F = C \times V_d \quad (1)$$

and V_d can be expressed by

$$V_d = \left(R_a + R_b + R_c\right)^{-1}. \quad (2)$$

Here, R_a is the aerodynamic resistance, R_b is the quasi-laminar boundary layer resistance, and R_c is the surface or canopy

resistance. In the three resistances, R_a is dependent on the meteorological conditions and it should be calculated for a range of atmospheric stabilities, and R_b is mainly about the gas own characteristic. R_c is quite complicated in inferential model and difficult for dry deposition calculation due to the different surface features and gas or particles species (Erisman and Pul Van 1994).

In this study we did not have enough equipment or suitable methods to calculate the dry deposition velocities at the ocean surface. In addition, studies on N dry deposition velocities above the ocean surface are very limited, so we decided to use the deposition velocities from the Chinese literature on the ocean. We therefore cited deposition velocities of the gases NH_3, HNO_3, and NO_2 from Zhang *et al* (2010) and those of particulate pNH_4^+ and pNO_3^- from Zhang *et al* (2004).

3. Results

3.1. Atmospheric concentrations of reactive N components

Atmospheric concentrations of reactive N components are shown in figure 2. Annual average NH_3 concentrations were 2.73, 3.50, 3.97, 7.34, 2.13, and 5.62 $\mu g\,N\,m^{-3}$ at sites DL, CD, LS, FH, FZ, and ZJ, respectively. The concentrations of NH_3 were higher at FH and ZJ than at the other sites because of the high level of agricultural activity. HNO_3 and NO_2 concentrations ranged from 0.46 to 1.22 $\mu g\,N\,m^{-3}$ and 3.10 to 7.19 $\mu g\,N\,m^{-3}$ across all six sites. The lowest concentrations of HNO_3 and NO_2 were observed at FZ and the highest were found at FH and CD, reflecting the weak effects of power plants, industry and transportation on the concentrations measured at FZ but strong effects on FH and CD because of the large population densities and advanced economic activities. Average pNO_3^- concentrations were 1.14–2.68 $\mu g\,N\,m^{-3}$ at the six sampling sites. The highest value was measured at CD and the lowest at FZ. Average concentrations of pNH_4^+ were 4.16, 4.45, 4.78, 4.07, 2.29, 3.30 $\mu g\,N\,m^{-3}$ at sites DL, CD, LS, FH, FZ, ZJ, respectively. Air concentrations of pNH_4^+ at the North coastal sites (DL, CD and LS) were almost twice of those at the Southern FZ site, whereas the concentrations of pNH_4^+ at FH and ZJ were close to the North coastal sites. Three North sampling sites located close to the North China Plain, an intensively managed agricultural region, and the higher pNH_4^+ concentrations in this area showed agricultural source impacts on secondary aerosols (e.g., NH_4^+-based $PM_{2.5}$).

3.2. Seasonal variation in reactive N concentrations

Table 2 shows the seasonal variation in reactive N concentrations at the six sampling sites. A peak NH_3 concentration was found in summer at all sites (except DL) because high temperatures together with N fertilization in summer induce high NH_3 emissions from various sources. The lowest concentration of NH_3 was observed in winter at all sampling sites. The air concentration of pNH_4^+ was highest in spring or winter. The results may be explained by low rainfall in the spring and winter, and in addition, coal consumption for heating in the winter and spring can also stimulate the formation of particulate NH_4^+. HNO_3 concentrations did not show notable seasonal variation across the six sampling sites. Peak concentrations of pNO_3^- were observed in winter or spring and lowest in the summer. Seasonal variation in pNO_3^- is similar to that of pNH_4^+ in air as mentioned above. The meteorology and heating stimulate higher pNO_3^- pollution especially in North China in winter. The pNO_3^- concentrations were 24.2% higher at coastal sites of North China (DL, CD and LS) than at sites of South China (FH, FZ and ZJ) in winter. Concentrations of NO_2 mainly peaked in winter or spring and had a close relationship with heating, especially in North China.

3.3. N wet deposition

Rainfall distribution showed seasonal and regional variations. South China sampling sites had more rainfall than the Northern sites. The latter had lesser or even no rain in winter and spring but the Southern sites experienced more rain in these two seasons. The inorganic N concentrations in rainwater were 0.46–1.67 $mg\,N\,L^{-1}$ for NO_3^-–N and 0.47–1.31 $mg\,N\,L^{-1}$ for NH_4^+–N (table 3). Nitrogen concentrations in rainwater followed the pattern in atmospheric reactive N concentrations. For example, CD and FZ had the highest and lowest inorganic N concentrations in rainwater in relation to the highest and lowest concentrations of atmospheric reactive N at the two sites, respectively. N wet deposition ranged from 14.2 to 25.2 $kg\,N\,ha^{-1}\,yr^{-1}$. N wet deposition rate was controlled by the N concentration in rainwater and the amount of annual rainfall. The NH_4^+/NO_3^- ratio was lower than 1.0 except at ZJ, so wet deposition of NO_3^-–N was slightly higher than that of NH_4^+–N in our study.

3.4. N dry deposition

Annual N dry deposition was 12.9, 16.9, 15.2, 23.1, 7.8 and 18.0 $kg\,N\,ha^{-1}$ at DL, CD, LS, FH, FZ, and ZJ sampling sites, respectively (figure 3(a)). The estimated dry deposition velocities of NH_3, HNO_3, NO_2, pNH_4^+ and pNO_3^- averaged 0.626, 0.63, 0.005 34, 0.27 and 0.27 $cm\,s^{-1}$, respectively, which were taken directly from (Zhang *et al* 2004, 2010). NH_3 and pNH_4^+ were the major parts in the N dry deposition because they have both higher concentrations and higher deposition velocities, and the total NH_3 and pNH_4^+ contribution to the dry deposition was 72.1–81.7%. FH had the highest N dry deposition rate because of the highest reactive N concentrations (especially NH_3 and NO_2). FZ had the lowest dry deposition rate because all reactive N components were very low at this site. In general, the N dry deposition rate is comparable to the N wet deposition in our study (except FZ). Given the wet N deposition, the annual total N deposition rates were 29.9, 32.8, 31.1, 44.6, 22.0, 43.2 $kg\,ha^{-1}\,yr^{-1}$ at DL, CD, LS, FH, FZ, and ZJ (figure 3(b)), respectively.

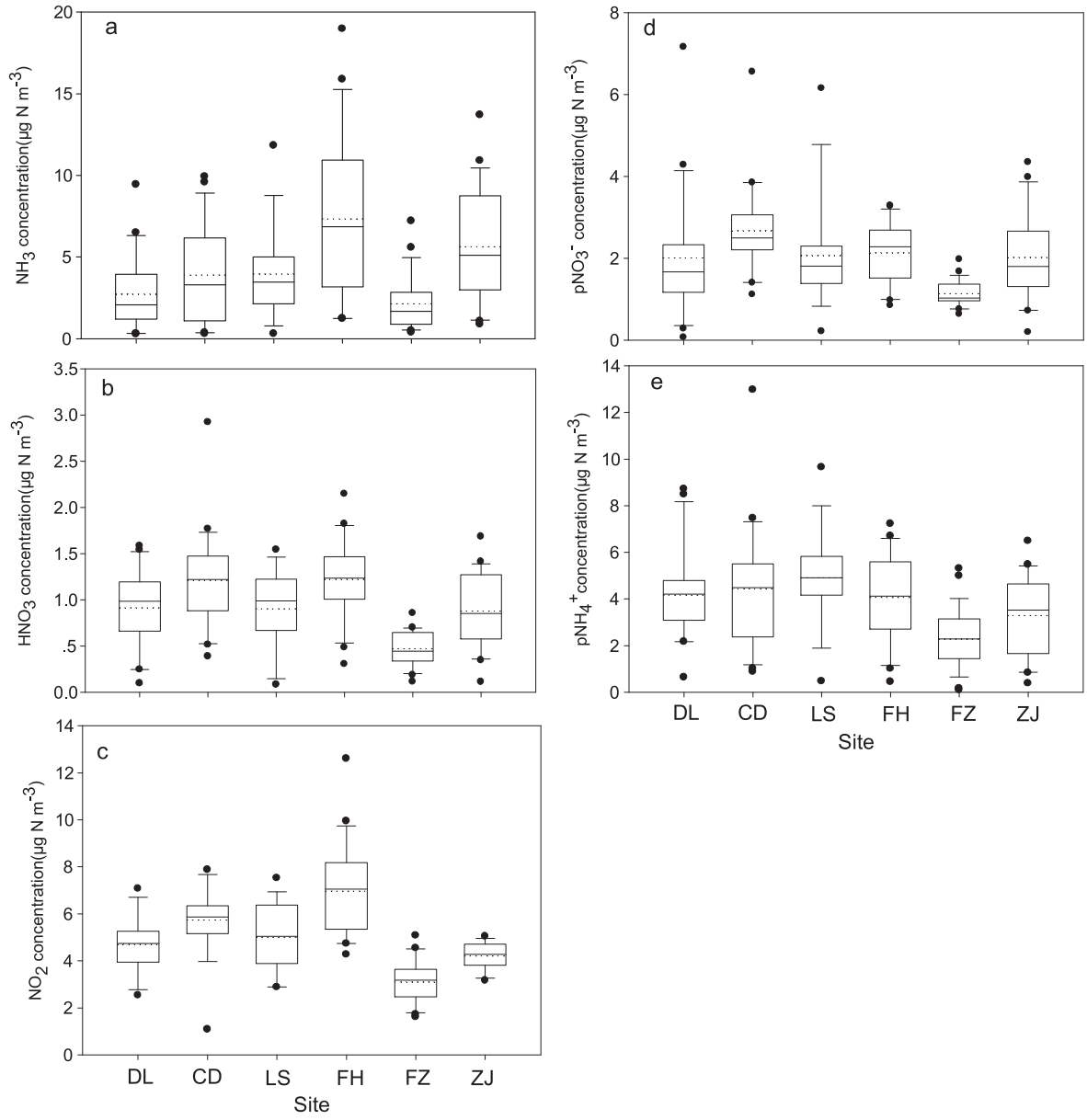

Figure 2. Atmospheric concentrations of reactive N ((a) NH_3, (b) HNO_3, (c) NO_2, (d) pNO_3^-, (e) pNH_4^+) at six sites during sampling periods. Solid line represents median values and dotted line represents average values.

4. Discussion

4.1. The atmospheric reactive N conditions in coastal areas of China

NH_3 and NO_x are two primary reactive N species in air which are emitted mainly from human activity. Rapid economic development in China has led to continuing increases in NH_3 and NO_x emissions since the 1980s (Liu *et al* 2013). However, the N emissions varied from region to region and also from season to season due to the large differences in population density, economic function, land use types and weather conditions. The NH_3 emission 'hot-spots' were in Hebei, Henan, Shandong and Jiangsu provinces (Clarisse *et al* 2009, Zhang *et al* 2010), while the NO_x emission 'hotspots' were in some well developed regions such as Jing-Jin-Ji (Beijing-Tianjin-Hebei) Region, the Yangtze River Delta and the Pearl River Delta (Richter *et al* 2005, Gu *et al* 2012). In this study the NH_3, HNO_3 and NO_2 concentrations were much lower than our previous results on the North China Plain (Shen *et al* 2009, Luo *et al* 2013), but are comparable to the results from three South China sampling sites in Hunan province (Shen *et al* 2013).

Atmospheric pNH_4^+, pNO_3^-, and pSO_4^{2-} are important components of secondary aerosols. Particulate pollution is a major public concern and there are many studies focusing on urban regions (Chan and Yao 2008). Our data show that atmospheric concentrations of pNH_4^+ and pNO_3^- or pSO_4^{2-} were significantly correlated (figures 4(a) and (b)). The pNO_3^-, pSO_4^{2-} and pNH_4^+ made an important contribution to the formation of secondary particulates (e.g., NH_4NO_3 and $(NH_4)_2SO_4$) and their transportation to the coastal sea. China

Table 2. Seasonal variation in atmospheric reactive N components across the six coastal sampling sites (mean ± SD, μg N m^{-3}).

	Site	Spring	Summer	Autumn	Winter
NH_3	DL	2.47 ± 2.46	3.80 ± 0.95	3.89 ± 2.91	1.12 ± 0.78
	CD	5.52 ± 3.28	6.65 ± 2.13	3.50 ± 1.31	0.77 ± 0.67
	LS	4.65 ± 0.94	6.86 ± 4.37	1.84 ± 1.52	1.82 ± 0.77
	FH	8.22 ± 4.01	11.88 ± 4.28	7.44 ± 4.75	2.84 ± 1.63
	FZ	1.78 ± 0.90	3.98 ± 1.94	1.39 ± 0.42	0.73 ± 0.38
	ZJ	6.81 ± 3.02	9.23 ± 3.11	5.59 ± 2.07	1.94 ± 0.97
pNH_4^+	DL	3.68 ± 1.71	3.55 ± 0.99	3.72 ± 1.33	5.47 ± 2.53
	CD	5.53 ± 4.50	5.07 ± 1.47	4.21 ± 2.02	3.30 ± 1.29
	LS	5.02 ± 1.40	3.28 ± 2.43	4.10 ± 1.09	7.18 ± 2.30
	FH	3.12 ± 1.69	3.48 ± 1.68	3.57 ± 1.94	5.69 ± 1.21
	FZ	2.74 ± 1.25	1.89 ± 1.78	2.23 ± 0.45	2.09 ± 1.17
	ZJ	2.56 ± 1.50	1.96 ± 1.98	4.29 ± 0.88	3.61 ± 2.12
HNO_3	DL	0.71 ± 0.49	0.72 ± 0.21	1.11 ± 0.31	1.03 ± 0.43
	CD	1.05 ± 0.47	1.05 ± 0.20	1.40 ± 0.32	1.27 ± 0.89
	LS	0.99 ± 0.16	0.78 ± 0.22	0.82 ± 0.55	0.78 ± 0.67
	FH	1.37 ± 0.26	1.09 ± 0.27	0.87 ± 0.52	1.56 ± 0.32
	FZ	0.50 ± 0.14	0.61 ± 0.13	0.36 ± 0.21	0.37 ± 0.18
	ZJ	0.93 ± 0.48	0.36 ± 0.21	0.97 ± 0.32	1.05 ± 0.29
pNO_3^-	DL	1.55 ± 1.14	1.44 ± 0.24	1.78 ± 0.78	3.12 ± 2.23
	CD	3.38 ± 1.75	2.17 ± 0.43	2.63 ± 0.91	2.33 ± 0.69
	LS	1.88 ± 0.41	1.49 ± 0.24	1.32 ± 1.05	3.89 ± 2.15
	FH	2.17 ± 0.67	1.55 ± 0.87	1.78 ± 0.70	2.76 ± 0.35
	FZ	1.30 ± 0.36	1.08 ± 0.30	1.06 ± 0.31	1.05 ± 0.19
	ZJ	1.63 ± 0.57	0.75 ± 0.51	1.95 ± 0.70	3.27 ± 0.89
NO_2	DL	5.45 ± 1.10	3.82 ± 0.78	4.20 ± 1.66	5.07 ± 1.25
	CD	6.21 ± 0.89	4.87 ± 0.43	5.51 ± 1.04	6.53 ± 0.87
	LS	5.74 ± 1.80	3.72 ± 0.74	4.12 ± 0.88	5.94 ± 0.50
	FH	7.11 ± 2.08	5.24 ± 0.74	6.75 ± 1.14	8.52 ± 2.07
	FZ	3.76 ± 0.60	3.40 ± 1.01	2.04 ± 0.52	2.93 ± 0.69
	ZJ	4.05 ± 0.94	4.36 ± 0.39	3.96 ± 0.53	4.49 ± 0.25

Table 3. Inorganic N concentrations in precipitation and wet deposition at the six coastal sampling sites.

Site	Rainfall N concentration (mg N L^{-1})				N wet deposition (kg N ha^{-1} yr^{-1})		
	(mm yr^{-1})	NO_3^-–N	NH_4^+–N	Total	NO_3^-–N	NH_4^+–N	Total
DL	660.8	1.36	1.21	2.57	9.01	7.98	16.99
CD	531.8	1.67	1.31	2.98	8.86	6.97	15.83
LS	731.4	1.15	1.02	2.17	8.45	7.44	15.89
FH	1120.6	1.04	0.88	1.92	11.7	9.86	21.56
FZ	1528.4	0.46	0.47	0.93	7.00	7.23	14.23
ZJ	1952.0	0.87	1.11	1.98	12.0	13.2	25.20

has made great progress in controlling particulate matter but concentrations remain high because industrial development has offset the PM control technology and the conditions of particulate pollution are even more problematic in the cities of North China (Wang and Hao 2012). Compared with particulate NH_4^+ and NO_3^- concentrations on the North China Plain (Luo *et al* 2013), the concentrations of pNH_4^+ and pNO_3^- at the six coastal sites were lower especially at one Southeast sampling site (FZ). China uses large amounts of coal which accounts for about 70% of its energy consumption. SO_4^{2-} is therefore one of the most important components in particulate matter (Chan and Yao 2008). The SO_4^{2-}/NO_3^- ratio is very low in this study (SO_4^{2-}/NO_3^- ratios were 0.48, 0.49, 0.69, 0.49, 0.87, 0.50 at DL, CD, LS, FH, FZ, and ZJ, respectively), reflecting the possibly higher contribution of the transportation sector and rapid urbanization to the present-day air pollution. Our results are consistent with recent reports of decreasing SO_4^{2-}/NO_3^- trends in Beijing and Shanghai (Shen *et al* 2011b, Huang *et al* 2012). Natural processes can also produce aerosols. Cusack *et al* (2012) found crustal material and marine aerosol comprising 9% and 2% respectively of the total sum of the chemical components at a sampling site in Spain. In addition, forest fires and volcanic eruption form large amounts of natural-source aerosols.

Regarding seasonal variation and taking NH_3 as an example, we know that fertilized soils, animal/human

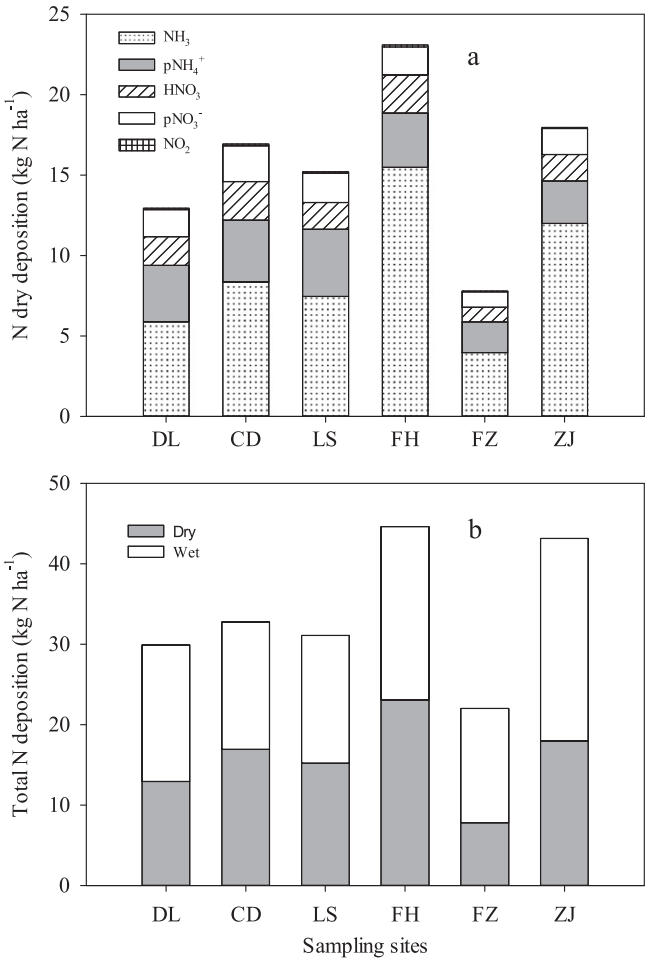

Figure 3. Atmospheric N dry deposition (a) and total deposition (b) rates at the sampling sites.

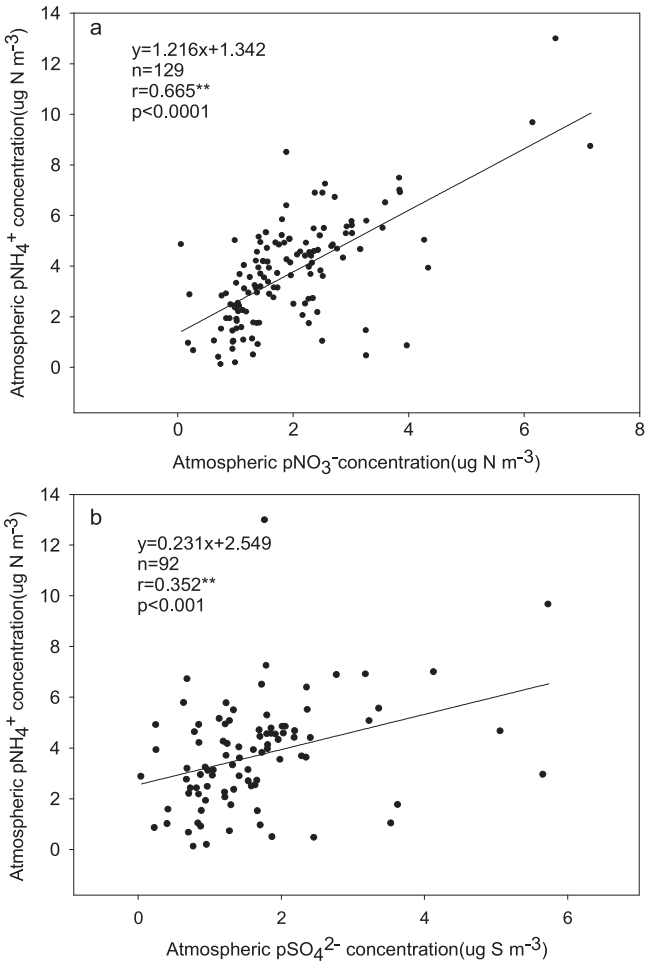

Figure 4. Relationship between atmospheric pNH_4^+ and pNO_3^- (a) and/or pSO_4^{2-} (b).

manures and biomass burning are major NH_3 emission sources worldwide. These emission sources have a close relationship with temperature and high temperatures stimulate NH_3 emission in summer (Shen *et al* 2011a). The oceans are important natural sources of NH_3 emissions Olivier *et al* (1998) and high temperatures also stimulate NH_3 emissions from the oceans in summer. Meteorological conditions may affect the air quality in the coastal sea in different seasons. The wind comes mainly from the sea in the summer and brings relatively clear air from the ocean which is also an explanation for the lower pNH_4^+ and pNO_3^- concentrations in summer. Wind comes mainly from the West or North in winter and the sampling sites were affected by the land sources. As a result, particulate pollution is usually higher in winter and spring. There are always sand storms from Inner Mongolia in spring and there can be long-range transport to the China seas affecting the air quality in this region and to a lesser extent the Yellow Sea followed by the Bohai Sea, the East China Sea, and the Northern South China Sea (Tan *et al* 2012).

Precipitation can remove various components from the atmosphere, so the precipitation N concentrations have a close relationship with the atmospheric concentrations of NH_3 and NH_4^+ (Xiao *et al* 2012). As reported by Liu *et al* (2013), inorganic N concentrations in precipitation show remarkable differences in different regions of China. The average concentration was 1.20 mg N L^{-1} for NH_4^+–N, and 0.97 mg N L^{-1} for NO_3^-–N at a South China site in Guangzhou city (Jia and Chen 2010). Chen and Mulder (2007) reported lower inorganic N concentrations in precipitation (NH_4^+–N 0.29–2.33 mg N L^{-1} and NO_3^-–N 0.20–1.11 mg N L^{-1}) at four South China sites in Hunan, Chongqing and Guizhou. Our study reflects the consistency of rainwater N concentrations with rainfall distribution in different regions. The North China sites had higher N concentrations in precipitation than the South China sites due to the lower rainfall and higher atmospheric reactive N concentrations (Zhang *et al* 2008). This study confirms the higher inorganic N concentrations in rainwater at coastal sites of North China than South China. The lower inorganic N concentration in rainwater at FZ in our study compares well with the inorganic N concentration in rainwater (1.74 mg N L^{-1}) in Xiamen (Chen *et al* 2011).

4.2. Impact of N deposition on the coastal ocean ecosystems

Nitrogen wet and dry deposition in coastal areas in our study was overall lower than that in intensive agricultural areas of China. For example, on the North China Plain, N wet and dry

deposition ranged from 60–102 kg N ha^{-1} yr^{-1} due to high air pollution and the inter-annual variability of rainfall (Pan *et al* 2012, Luo *et al* 2013). Nitrogen wet deposition in the Taihu Lake region and Shanghai area in East China was estimated to be about 30 kg N ha^{-1} yr^{-1} (Xie *et al* 2008) and 58 kg N ha^{-1} yr^{-1} (Mei and Zhang 2007), respectively. Jia and Chen (2010) reported an N wet deposition of 52.8 kg N ha^{-1} yr^{-1} at a South urban sampling site of Guangzhou. However, N wet deposition on the lower Liaohe River Plain in Northeast China was only 14.5 kg N ha^{-1} yr^{-1} (Yu *et al* 2011) and close to our results.

For the coastal sea area, streams and rivers are additional nutrient sources to estuarine and coastal marine environments. The inputs of N and P increased rapidly by erosion from arable lands or carrying human wastewater, so the coastal sea is more affected by human activity than only by air pollution (Smith *et al* 1999). Atmospheric N deposition represents a long-term low level fertilization effect for the ocean and has consequences for the natural biogeochemical cycles of N and increases the productivity of the oceans (Duce *et al* 2008). Compared with the riverine N input into the coastal ocean, N deposition may have long range impacts on the open ocean downwind of the primary source regions, especially in Eastern North America, Europe, and South and East Asia (Doney *et al* 2007). China is one of the hotspots of global reactive N emissions and deposition (Galloway *et al* 2008, Liu *et al* 2013). Several studies have quantified potential reactive N long range transport. For example, a modeling study showed that the high emissions of reactive N in China made a significant contribution to Japan's HNO_3 deposition through long-range transport (Holloway *et al* 2002). The Yellow Sea regions showed high N deposition through long-range transport from East Asia (Kim *et al* 2010). Total N deposition averaged 33.9 kg N ha^{-1} yr^{-1} for all the sampling sites in this study. If we consider this to be representative of N deposition for the sea area, it makes a significant contribution in addition to the river or the groundwater N entering the oceans. Assuming an annual mean N deposition of 33.9 kg N ha^{-1}, the total N deposition into the whole Chinese coastal seas (total area approx. 0.4 million km^2, calculating from 18 000 km length of boundary line of territorial waters with 22 km width of territorial waters) can amount to 1.36 Tg N yr^{-1}. It is a large N nutrient input from atmospheric deposition, which is comparable to inorganic N output of 1.61 Tg N yr^{-1} from the Yangtze River to the East China Sea (Yan *et al* 2010) and estimated feed N input (~1.5 Tg N yr^{-1}) from coastal aquaculture (www.zg3n.com.cn/2012/0904/15059.html). Although no systematic studies show the total N input from riverine source, aquaculture and deposition (three major N sources in coastal zones), the contribution of N deposition to Chinese coastal N input (amounting to about 30% of total N input) should not be neglected. Such high levels of N deposition in particular NH_4^+/NH_3 deposition may lead to secondary N_2O emissions either from soils or marine ecosystems (Matson *et al* 2002, Duce *et al* 2008), due to nitrification and denitrification. Our monitoring results are 3–8 times higher than the modeled N deposition rates (2.5–11 kg N ha^{-1} yr^{-1}) in the East China Sea (Zhang *et al* 2010). One possible explanation may be that we focus on the coastal sea and atmospheric reactive N concentrations and deposition show a decreasing gradient downward from the shore and are therefore significantly lower for the whole sea area. Another possibility is that the modeling results underestimate N wet and dry deposition in the coastal areas.

In addition, the coastal ocean environment is also affected by P and iron inputs and other complex chemical process (Deutsch *et al* 2007), so it is quite complicated to quantify the environmental impact of N deposition to the coastal ocean and further research is also needed to quantify all the nutrient fluxes from mainland China to the ocean. Nitrogen dry deposition velocities were taken directly from the literature (e.g., Zhang *et al* 2004, 2010) and are therefore highly uncertain, leading to uncertainties for the dry deposition rates in this study, and this needs more accurate estimation in future studies.

5. Conclusion

This study provides an updated evaluation of present-day atmospheric reactive N conditions in Chinese coastal regions. Our data show lower atmospheric reactive N concentrations in the coastal area than previous results in North China but large rates of N dry and wet deposition. The annual total N deposition ranged from 22.0 to 44.6 kg N ha^{-1} and averaged 33.9 kg N ha^{-1} at the six sampling sites along the coastal zones. Average N dry deposition account for 45.4% of the total deposition demonstrating that it is important part of the total deposition. The significant relationships between pNH_4^+ and pNO_3^- and/or pSO_4^{2-} concentrations suggest that pollution transportation may make an important contribution to the formation of secondary aerosols (including $PM_{2.5}$) in Chinese coastal regions. Ratios of pSO_4^{2-}/pNO_3^- were very low in this study reflecting a large contribution of the transportation sector to current air pollution in China. High levels of N deposition in the coastal seas remind us to pay more attention to the impacts of atmospheric reactive N pollution and deposition on the sensitive coastal zones and surrounding marine ecosystems.

Acknowledgements

We thank Dr Peter Christie for correcting the English of the manuscript, Ms Zong Xiaoyan for analyzing N wet deposition and Mr Chang Yunhua for helping us to draw the monitoring site distribution figure. This work was supported by the Chinese National Basic Research Program (2014CB954202), the Chinese National Fund for Distinguished Scholars and the Innovative Group Grant from the NSFC (31121062).

References

Allen A G, Machado C M D and Cardoso A A 2011 Measurements and modeling of reactive nitrogen deposition in Southeast Brazil *Environ. Pollut.* **159** 1190–7

Chan C K and Yao X H 2008 Air pollution in mega cities in China *Atmos. Environ.* **42** 1–42

Chen N W, Hong H S, Huang Q J and Wu J Z 2011 Atmospheric nitrogen deposition and its long-term dynamics in a southeast China coastal area *J. Environ. Manage.* **92** 1663–7

Chen X Y and Mulder J 2007 Atmospheric deposition of nitrogen at five subtropical forested sites in South China *Sci. Total Environ.* **378** 317–30

Clarisse L, Clerbaux C, Dentener F, Hurtmans D and Coheur P F 2009 Global ammonia distribution derived from infrared satellite observations *Nat. Geosci.* **2** 1–5

Conley D J, Paerl H W, Howarth R W, Boesch D F, Seitzinger S P, Havens K E, Lancelot C and Likens G E 2009 Controlling eutrophication: nitrogen and phosphorus *Science* **323** 1014–5

Cui S H, Shi Y L, Groffman P M, Schlesinger W H and Zhu Y G 2013 Centennial-scale analysis of the creation and fate of reactive nitrogen in China (1910–2010) *Proc. Natl. Acad. Sci.* **110** 2052–7

Cusack M, Alastuey A, Pérez N, Pey J and Querol X 2012 Trends of particulate matter ($PM_{2.5}$) and chemical composition at a regional background site in the western mediterranean over the last nine years (2002–2010) *Atmos. Chem. Phys.* **12** 8341–57

Deutsch C, Sarmiento J L, Sigman D M, Gruber N and Dunne J P 2007 Spatial coupling of nitrogen inputs and losses in the ocean *Nature* **445** 163–7

Doney S C, Mahowald N, Lima L, Feely R A, Mackenzie F T, Lamarque J and Rasch P J 2007 Impact of anthropogenic atmospheric nitrogen and sulfur deposition on ocean acidification and the inorganic carbon system *Proc. Natl. Acad. Sci.* **104** 14580–5

Duce R A *et al* 2008 Impacts of atmospheric anthropogenic nitrogen on the open *Ocean Sci.* **320** 893–7

Erisman J W, Galloway J N, Seitzinger S, Bleeker A and Butterbach-Bahl K 2011 Reactive nitrogen in the environment and its effect on climate change *Curr. Opin. Environ. Sustain.* **3** 281–90

Erisman J W, Galloway J N, Seitzinger S, Bleeker A, Dise N B, Petrescu A M R, Leach A M and de Vries W 2013 Consequences of human modification of the global nitrogen cycle *Phil. Trans. R. Soc.* B **368** 20130116

Erisman J W and Pul Van A 1994 Parameterization of surface resistance for the quantification of atmospheric deposition of acidifying pollutants and ozone *Atmos. Environ.* **28** 2595–607

Flechard C R *et al* 2011 Dry deposition of reactive nitrogen to European ecosystems: a comparison of inferential models across the NitroEurope network *Atmos. Chem. Phys.* **11** 2703–28

Galloway J N, Townsend A, Erisman J W, Bekunda M, Cai Z C, Freney J R, Martinelli L A, Seitzinger S P and Sutton M A 2008 Transformation of the nitrogen cycle: recent trends, questions, and potential solutions *Science* **320** 889–92

Gu B J, Ge Y, Ren Y, Xu B, Luo W D, Jiang H, Gu B H and Chang J 2012 Atmospheric reactive nitrogen in China: Sources, recent trends and damage costs *Environ. Sci. Technol.* **46** 9240–7

Guo J H, Liu X J, Zhang Y, Shen J L, Han W X, Zhang W F, Christie P, Goulding K, Vitousek P and Zhang F S 2010 Significant soil acidification in major Chinese croplands *Science* **327** 1008–10

Holloway T, Levy H II and Carmichael G 2002 Transfer of reactive nitrogen in Asia: Development and evaluation of a source–receptor model *Atmos. Environ.* **36** 4251–64

Howarth R W 2008 Coastal nitrogen pollution: a review of sources and trends globally and regionally *Harmful Algae* **8** 14–20

Huang K *et al* 2012 Typical types and formation mechanisms of haze in an Eastern Asia megacity, Shanghai *Atmos. Chem. Phys.* **12** 104–24

Jia G D and Chen F J 2010 Monthly variations in nitrogen isotopes of ammonium and nitrate in wet deposition at Guangzhou, South China *Atmos. Environ.* **44** 2309–15

Kim J Y, Ghim Y S, Lee S B, moon K C, Shim S G, Bae G N and Yoon S C 2010 Atmospheric deposition of nitrogen and sulfur in the Yellow Sea region: significance of long-range transport in East Asia *Water Air Soil Pollut.* **205** 259–72

Kim T W, Lee K, Najjar R G, Jeong H D and Jeong H J 2011 Increasing N abundance in the North Western Pacific Ocean due to atmospheric nitrogen deposition *Science* **334** 505–9

Liu X J *et al* 2013 Enhanced nitrogen deposition over China *Nature* **494** 459–62

Liu X J, Duan L, Mo J M, Du E Z, Shen J L, Lu X K, Zhang Y, Zhou X B, He C E and Zhang F S 2011 Nitrogen deposition and its ecological impact in China: an overview *Environ. Pollut.* **159** 2251–64

Luo X S *et al* 2013 An evaluation of atmospheric N_r pollution and deposition in North China after the Beijing Olympics *Atmos. Environ.* **74** 209–16

Matson P, Lohse K A and Hall S J 2002 The globalization of nitrogen deposition: consequences for terrestrial ecosystems *Ambio* **31** 113–9

Mei X Y and Zhang X F 2007 Nitrogen in wet deposition in Shanghai area and its effects on agriculture ecosystem *Chin. J. Eco-Agric.* **15** 16–8

Olivier J G J, Bouwman A F, Vander H K W and Berdowski J J M 1998 Global air emission inventories for anthropogenic sources of NO_x, NH_3 and N_2O in 1990 *Environ. Pollut.* **102** 135–48

Pan Y P, Wang Y S, Tang G Q and Wu D 2012 Wet and dry deposition of atmospheric nitrogen at ten sites in Northern China *Atmos. Chem. Phys.* **12** 6515–35

Rattray G and Sievering H 2001 Dry deposition of ammonia, nitric acid, ammonium, and nitrate to alpine tundra at Niwot Ridge, Colorado *Atmos. Environ.* **35** 1105–9

Richter A, Burrows J P, Nüß H, Granier C and Niemeier U 2005 Increase in tropospheric nitrogen dioxide over China observed from space *Nature* **437** 129–32

Seitzinger S P *et al* 2010 Global river nutrient export: a scenario analysis of past and future trends *Glob. Biogeochem. Cycles* **24** GB0A08

Shen J L, Li Y, Liu X J, Luo X S, Tang H, Zhang Y Z and Wu J S 2013 Atmospheric dry and wet nitrogen deposition on three contrasting land use types of an agricultural catchment in subtropical central China *Atmos. Environ.* **67** 415–24

Shen J L, Liu X J, Zhang Y, Fangmeier A, Goulding K and Zhang F S 2011a Atmospheric ammonia and particulate ammonium from agricultural sources in the North China plain *Atmos. Environ.* **45** 5033–41

Shen J L, Tang A H, Liu X J, Fangmeier A, Goulding K T W and Zhang F S 2009 High concentrations and dry deposition of reactive nitrogen species at two sites in the North China Plain *Environ. Pollut.* **157** 3106–13

Shen J L, Tang A H, Liu X J, Kopsch J, Fangmeier A, Goulding K and Zhang F S 2011b Impacts of pollution controls on air quality in Beijing during the 2008 Olympic Games *J. Environ. Qual.* **40** 37–45

Smith V H, Tilman G D and Nekola J C 1999 Eutrophication: impacts of excess nutrient inputs on freshwater, marine, and terrestrial ecosystems *Environ. Pollut.* **110** 179–96

Tan S C, Shi G Y and Wang H 2012 Long-range transport of spring dust storms in Inner Mongolia and impact on the China seas *Atmos. Environ.* **46** 299–308

Wang S X and Hao J M 2012 Air quality management in China: issues, challenges, and options *J. Environ. Sci.* **24** 2–13

Xiao X H, Xiao H Y, Long A M and Wang Y L 2012 Who controls the monthly variations of NH_4^+ nitrogen isotope composition in precipitation? *Atmos. Environ.* **54** 201–6

Xie Y X, Xiong Z Q, Xing G X, Yan X Y, Shi S L, Sun G Q and Zhu Z L 2008 Source of nitrogen in wet deposition to a rice agroecosystem at Tai lake region *Atmos. Environ.* **42** 5182–92

Yan W J, Magorga E, Li X Y, Seitzinger S P and Bouwman A F 2010 Increase anthropogenic nitrogen inputs and riverine DIN exports from Changjiang River basin under changing human pressures *Glob. Biogeochem. Cycles* **24** GB0A06

Yu W T, Jiang C M, Ma Q, Xu Y G, Zou H and Zhang S C 2011 Observation of the nitrogen deposition in the lower Liaohe River Plain, Northeast China and assessing its ecological risk *Atmos. Res.* **101** 460–8

Zhang Y, Liu X J, Fangmeier A, Goulding K T W and Zhang F S 2008 Nitrogen inputs and isotopes in precipitation in the North China Plain *Atmos. Environ.* **42** 1436–48

Zhang Y, Wang T J, Hu Z Y and Xu C K 2004 Temporal variety and spatial distribution of dry deposition velocities of typical air pollutants over different landuse types *Clim. Environ. Res.* **9** 591–604

Zhang Y, Yu Q, Ma W C and Chen L M 2010 Atmospheric deposition of inorganic nitrogen to the Eastern China seas and its implications to marine biogeochemistry *J. Geophys. Res.* **115** 1–10